

Effect of Addition of Ameliorative Materials on the Distribution of As, Cd, Pb, and Zn in Extractable Soil Fractions*

J. SZÁKOVÁ**, P. TLUSTOŠ, D. PAVLÍKOVÁ, A. HANČ, and M. BATYSTA

Department of Agrochemistry and Plant Nutrition, Czech University of Agriculture, CZ-165 21 Prague, Czech Republic e-mail: szakova@af.czu.cz

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The effects of lime, limestone, and zeolite addition on the availability of As, Cd, Pb, and Zn in three contaminated soils were investigated in a pot experiment after four vegetation periods of spring wheat, spring barley, and oat. The results showed different responses of extractable element portions to soil amendment when 0.01 mol dm⁻³ aqueous $CaCl_2$ was applied as a soil extraction agent. Substantial differences were evident among the investigated elements as well as among the individual soil treatments. Except natural zeolite, the ability of ameliorative materials to redistribute cadmium and zinc from a soil solution into less mobile but labile soil fractions was observed. The lead availability was less affected and the extractability of arsenic even increased in some of the treated pots. Moreover, the availability of arsenic was more affected by different characteristics of experimental soils than by individual soil treatments. It was found that these treatments can be applied neither for multicontaminated nor for all the soil types. The soil treatments had a lower effect on the less mobile soil fractions.

Keywords: potentially toxic elements, contaminated soil, liming, zeolite, immobilization

INTRODUCTION

The immobilization of toxic elements in soil via alteration of one or more soil characteristics (pH, sorption complex, content and composition of humic substances and content of Fe/Mn oxides) can significantly minimize element uptake by crops planted in soils with elevated heavy metal content and improve the quality of food production. Liming has been applied for a long time to increase soil pH and subsequently to decrease metal uptake by plants with respect to soil characteristics and behavior of individual elements in soil. Zeolites both natural (clinoptilolite, philipsite, *etc.*) and synthetic belong to the most effective mineral amendments reducing heavy metal transfer to plants [1].

Effective immobilizing agents for fixation of elements in soil suitable for *in situ* remediation of soils contaminated by potentially toxic elements were recently reviewed by *Guo et al.* [2]. The effectivity of CaO was emphasized in this regard because of its solubility and availability for reactions and large increase of soil pH. If the immobilization should be used as an effective soil remediation strategy, its long-term stability must be carefully monitored and assessed. Moreover, the results of pot experiments are not fully applicable in the field conditions [3]. The decrease of the mobility of cadmium, zinc, and lead in limed soil and effective decrease of their element uptake by several crops was intensively investigated and confirmed in both pot and field conditions [4—6].

A natural zeolite, clinoptilolite, was tested by *Chlopecka* and *Adriano* [7] to immobilize metals and decrease their uptake by maize (*Zea mays*) and barley (*Hordeum vulgare*) in an artificially contaminated soil. A substantial influence of soil pH and type of ameliorant on the chemical form and bioavailability of the metals was observed. Already low doses of zeolite (15 g kg⁻¹) reduced significantly the uptake of Cd and Pb by crops in most cases. *Madrid et al.* [8] compared different inorganic amendments including acid zeolite, sodium zeolite, slovakite, apatite in four urban soils using two doses (1 mass % and 5 mass %) and incubation lasting 1 year. Different responses were observed for individual amendments and/or elements.

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^{**}The author to whom the correspondence should be addressed.

a .1				Mass fraction/(mg kg^{-1})				
5011	Name and Source	fraction/%	рн	As	Cd	Pb	Zn	
А	Fluvisol from Litavka	4.4	5.8	190	57.9	5997	7453	
В	Cambisol from Příbram	2.1	6.0	31.7	7.14	2174	270	
С	Cambisol from Příbram	1.9	5.7	36.9	7.50	1747	237	

 Table 1. Basic Characteristics and Investigated Element Contents in Soil Samples

Usman et al. [9] observed that the labile soil fractions of Cd, Cu, Ni, Pb, and Zn and as well as the content of these elements in wheat plants were noticeably reduced after the addition of 2 % Na- or Ca-bentonites. Furthermore, the element contents in shoots, with the exception of Zn, were reduced below the phytotoxicity range and the shoot dry-matter production was significantly increased. Querol et al. [10] also confirmed that a zeolitic material considerably decreased the leaching of Cd, Co, Cu, Ni, and Zn in field experiments.

Single and sequential extraction methods are suitable for an evaluation of element distribution into individual soil fractions after experimental soil amendment by potentially risk elements [11] as well as for evaluation of remediation potential for these elements [12]. However, large diversity of sequential extraction schemes concerning the extraction reagents, operating conditions, and number of stages involved were developed and small changes in the experimental conditions (e.g. pH, temperature, contact time, solid to extractant volume ratio, particle size, sample pretreatment) can originate considerable variations in the fractionation [13, 14]. Single soil extraction procedures were recently evaluated by Menzies et al. [15]. The authors confirmed the suitability of neutral salt extractants $(0.01 \text{ mol } dm^{-3} \text{ CaCl}_2, 0.1 \text{ mol } dm^{-3} \text{ NaNO}_3)$ for the assessment of the available pool of elements in soil.

In our investigation, the effects of lime, limestone, and zeolite addition to the soils contaminated with different levels of As, Cd, Pb, and Zn were tested in pot experiments with simulated crop management. The ameliorative materials were added once at the beginning of the experiments. Since the long-term stability of element immobilization in contaminated soils can be useful for the design of remediation strategies, the long-term effects of these treatments were evaluated after four subsequent vegetation periods.

EXPERIMENTAL

Three soils containing 32—190 mg kg⁻¹ As, 7.1— 58 mg kg⁻¹ Cd, 1747—5997 mg kg⁻¹ Pb, and 237— 7453 mg kg⁻¹ Zn, respectively (Table 1) were used in pot experiments. Fluvisol from the alluvium of the Litavka river, Czech Republic was heavily polluted by wastes from smelter setting pits. Two types Cambisol soils were moderately contaminated by the atmospheric emissions from the same smelter. Mining and metallurgical activities in this area led to the enhancement of As, Cd, and Zn contents in soil due to high contents of trace elements in the parent rock [16]. Ameliorative materials were added into the pots before sowing in the following amounts per kg of a soil: 3 g CaO, 5.36 g CaCO₃ (both Lach-Ner Ltd., Czech Republic), 20 g of natural zeolite (Hungary), and 20 g of synthetic zeolite (Institute of Chemical Technology, Prague, Czech Republic).

Spring wheat cultivar Aranka, spring barley cultivar Jaspis, oat cultivar Zlaťák, and again spring wheat cultivar Aranka were planted in the pots for four subsequent vegetation periods. The pots containing 5 kg of air-dried and sieved (10 mm sieve) soil were kept in an outdoor weather-controlled vegetation hall. Each experiment was carried out in four replicates. The plants were regularly watered by deionized water and soil moisture was kept at 60 % of its maximal waterholding capacity. Wheat and barley plants were harvested in full maturity after 100 and 90 days, respectively. Oat was harvested after 70 days of planting. After each vegetation period, the soils were discharged from the pots to the plastic bags and kept over autumn and winter in a cold and dry place.

The total contents of the elements in the soils were determined before vegetation in the digests obtained by the following two-step decomposition procedure: 0.5 g of sample was decomposed by dry ashing in Apion Dry Mode Mineralizer. The ash was then decomposed in a mixture of HNO_3 and HF, evaporated to dryness at $160 \,^{\circ}$ C and dissolved in diluted aqua re*qia* [17]. A certified reference material RM 7001 Light Sandy Soil was applied for the quality assurance of analytical data. After the fourth vegetation period, the soil samples were collected from each pot, air-dried at 20 °C, ground in a mortar, and passed through a 2 mm plastic sieve. For the determination of the mobile portions of the elements in the soil samples, sample aliquots were extracted with a 0.01 mol dm^{-3} CaCl₂ aqueous solution using the ratio of 1 g of soil per 10 cm^3 of solvent for 6 h [18]. A standardized sequential analytical procedure [19] developed by the Institute for Reference Materials and Measurements was also applied for the determination of: i) exchangeable soil fraction (extractable by $0.11 \text{ mol } \text{dm}^{-3}$ acetic acid, at the soil mass to the volume of extraction solvent ratio of 1 g to 20 cm³), ii) fraction bound on Fe-Mn oxides (extractable by $0.1 \text{ mol dm}^{-3} \text{ NH}_2 \text{OH} \cdot \text{HCl}, 1 \text{ g of}$

Soil	Treatment	Mass fraction/(mg kg ⁻¹)				
		As	Cd	Pb	Zn	
А	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{c} 0.595 \pm 0.125^{ab} \\ 0.744 \pm 0.248^{b} \\ 0.492 \pm 0.154^{ab} \\ 0.387 \pm 0.137^{a} \\ 0.422 \pm 0.146^{a} \end{array}$	$\begin{array}{l} 12.7\pm 0.3^d\\ 1.40\pm 0.09^a\\ 2.19\pm 0.04^b\\ 11.2\pm 0.3^c\\ 1.30\pm 0.09^a\end{array}$	$\begin{array}{c} 1.25 \pm 0.19^{bc} \\ 1.48 \pm 0.10^c \\ 0.899 \pm 0.321^{ab} \\ 0.827 \pm 0.143^a \\ 0.975 \pm 0.233^{ab} \end{array}$	$\begin{array}{c} 691 \pm 19^{d} \\ 37.3 \pm 2.3^{a} \\ 64.6 \pm 1.6^{b} \\ 625 \pm 24^{c} \\ 59.0 \pm 2.7^{ab} \end{array}$	
В	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{c} 0.392 \pm 0.080^{bc} \\ 0.464 \pm 0.058^c \\ 0.411 \pm 0.096^{bc} \\ 0.293 \pm 0.040^{ab} \\ 0.193 \pm 0.052^a \end{array}$	$\begin{array}{c} 0.952\pm 0.043^d\\ 0.050\pm 0.003^a\\ 0.169\pm 0.023^b\\ 0.689\pm 0.019^c\\ 0.023\pm 0.003^a\end{array}$	$\begin{array}{c} 0.721 \pm 0.117^{bc} \\ 0.392 \pm 0.054^{a} \\ 0.499 \pm 0.106^{a} \\ 0.819 \pm 0.166^{c} \\ 0.577 \pm 0.079^{ab} \end{array}$	$\begin{array}{c} 16.1 \pm 1.5^{d} \\ 0.478 \pm 0.038^{a} \\ 2.01 \pm 0.39^{b} \\ 7.60 \pm 0.33^{c} \\ 0.075 \pm 0.021^{a} \end{array}$	
С	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 0.176 \pm 0.061^{bc} \\ 0.141 \pm 0.033^{ab} \\ 0.086 \pm 0.045^{a} \\ 0.230 \pm 0.020^{cd} \\ 0.264 \pm 0.046^{d} \end{array}$	$\begin{array}{c} 1.06 \pm 0.03^c \\ 0.007 \pm 0.004^a \\ 0.014 \pm 0.004^a \\ 0.951 \pm 0.044^b \\ 0.027 \pm 0.004^a \end{array}$	$\begin{array}{c} 1.07 \pm 0.05^{b} \\ 0.378 \pm 0.068^{a} \\ 0.392 \pm 0.154^{a} \\ 0.919 \pm 0.142^{b} \\ 0.216 \pm 0.081^{a} \end{array}$	$\begin{array}{c} 4.37 \pm 1.50^b \\ 0.035 \pm 0.036^a \\ 0.024 \pm 0.016^a \\ 4.12 \pm 0.29^b \\ 0.053 \pm 0.004^a \end{array}$	

Table 2. Element Portions Extractable with 0.01 mol dm^{-3} CaCl₂

The mean values for one component and one soil sample denoted with the same letter (a-d) did not differ at a level of $\alpha = 0.05$.

spoil per 20 cm³ of solvent), and iii) organically bound soil fractions (extractable by 8.8 mol dm⁻³ H₂O₂ + 1 mol dm⁻³ CH₃COONH₄, using the ratio of 1 g of soil per 50 cm³ of solvent).

Each extraction was carried out in five replicates when all chemicals used were of electronic grade purity and purchased from Analytika and Lach-Ner Ltd., Czech Republic. Hettich Universal 30 RF (Germany) equipment was used for the centrifugation of the reaction mixture at 3000 min⁻¹ (460 g) for 10 min at the end of each extraction step. Supernatants were kept at 6 °C before measurements. Blank extracts were prepared and analyzed in the same way as soil extracts. The soil pH was deduced on the basis of extracts obtained by contacting soil samples with 0.01 mol dm⁻³ aqueous CaCl₂ (using the ratio of 1 g of soil per 10 cm³ of extraction solvent) [18]. The content of oxidizable carbon in soil was determined colorimetrically according to Sims and Haby [20].

The total contents of arsenic, cadmium, lead, and zinc in the soil digests and in soil extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN VistaPro, Varian, Australia). Low levels of arsenic were determined by a continuous hydride generation technique using a Varian SpectrAA-300 (Australia) atomic absorption spectrometer equipped with hydride generator VGA-76. The element contents in soil extracts from individual pots were evaluated by ANOVA (Statgraphics 5.1plus) at the significance level $\alpha = 0.05$.

RESULTS AND DISCUSSION

Individual soil amendments resulted in different changes in soil pH. Whereas the natural zeolite did not affect the soil pH, the application of the synthetic zeolite increased the pH of the soils A, B, and C to 6.6 \pm 0.03, 6.8 \pm 0.1, and 6.6 \pm 0.05, respectively. The effect of liming on the soil pH level was even more significant. The pH of the soils reached the values of 6.8 \pm 0.03, 6.9 \pm 0.02, and 7.0 \pm 0.03, respectively when they were treated with limestone. Even higher values, 7.3 \pm 0.04, 7.4 \pm 0.03, and 7.3 \pm 0.05, respectively, were reached when the soils were lime-treated. The pH levels remained stable during all four vegetation periods.

Table 2 summarizes the portions of individual elements extractable with $0.01 \text{ mol } \text{dm}^{-3} \text{ CaCl}_2$. Significant differences in the availability of these elements are evident. Neutral salts solutions such as 0.01 mol dm^{-3} CaCl₂ simulate plant-available portion of elements in the soils. The extractable portions of elements sometimes correlate with their uptake by plants [21, 22]. The portion of extractable lead did not exceed 0.05 %of the total soil lead content regardless of the experimental soil. The response of available lead was different in individual soils. For the soil A, only lime showed no effect on the lead availability whereas for the soils B and C the extractability of lead decreased except for the amendment by the natural zeolite. In the case of arsenic, the extractability varied between 0.2 % (soil A) and 1.5 % (soil B) and the effect of liming was negligible. For the soil B, it even tended to increase the arsenic availability. A positive effect was observed for natural zeolites for soil B while other treatments did not show any influence.

The extractability of Cd and Zn was much higher than that of As and Pb. The extractable portion of cadmium (for control variants 21 % at soil A, 13 % at soil B, and 14 % at soil C) exceeded the portion of

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Table 3. Element Portions Extractable Using SM&T Sequential Extraction Procedure. Fraction 1 – Exchangeable (Extractablewith $0.11 \mod dm^{-3}$ Acetic Acid)

C - 11	Treatment	Mass fraction/(mg kg^{-1})				
5011		As	Cd	Pb	Zn	
А	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 1.91 \pm 0.15^{a} \\ 2.13 \pm 0.43^{a} \\ 2.00 \pm 0.34^{a} \\ 1.61 \pm 0.23^{a} \\ 2.08 \pm 0.26^{a} \end{array}$	$\begin{array}{l} 42.6 \pm 1.1^{b} \\ 39.7 \pm 0.4^{ab} \\ 39.5 \pm 1.1^{ab} \\ 36.4 \pm 5.6^{a} \\ 41.7 \pm 1.8^{b} \end{array}$	$\begin{array}{c} 193 \pm 7^c \\ 165 \pm 4^b \\ 156 \pm 11^b \\ 105 \pm 9^a \\ 197 \pm 2^c \end{array}$	$\begin{array}{l} 3347 \pm 67^{d} \\ 3095 \pm 28^{bc} \\ 3111 \pm 26^{cd} \\ 2847 \pm 309^{ab} \\ 2645 \pm 49^{a} \end{array}$	
В	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{c} 3.55 \pm 0.22^{b} \\ 4.53 \pm 0.17^{c} \\ 5.05 \pm 0.60^{c} \\ 3.65 \pm 0.19^{b} \\ 0.820 \pm 0.141^{a} \end{array}$	$\begin{array}{c} 4.15 \pm 0.19^c \\ 2.81 \pm 0.09^b \\ 4.47 \pm 0.69^d \\ 3.80 \pm 0.19^c \\ 0.961 \pm 0.141^a \end{array}$	$\begin{array}{c} 42.7 \pm 3.2^{b} \\ 32.5 \pm 0.3^{a} \\ 51.9 \pm 9.9^{c} \\ 32.0 \pm 1.8^{a} \\ 83.1 \pm 1.2^{d} \end{array}$	$\begin{array}{l} 108 \pm 13^c \\ 65.2 \pm 11.7^b \\ 148 \pm 43^d \\ 57.9 \pm 1.6^{ab} \\ 21.9 \pm 1.5^a \end{array}$	
С	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{c} 2.20 \pm 0.23^{bc} \\ 3.12 \pm 0.36^d \\ 2.57 \pm 0.27^c \\ 2.14 \pm 0.14^b \\ 0.547 \pm 0.111^a \end{array}$	$\begin{array}{c} 2.35 \pm 0.23^{bc} \\ 3.26 \pm 0.36^d \\ 2.71 \pm 0.27^c \\ 2.29 \pm 0.14^b \\ 0.693 \pm 0.111^a \end{array}$	$\begin{array}{c} 44.4 \pm 1.7^{b} \\ 30.3 \pm 0.8^{a} \\ 27.2 \pm 0.3^{a} \\ 28.6 \pm 1.6^{a} \\ 52.6 \pm 3.2^{c} \end{array}$	$\begin{array}{l} 21.9 \pm 1.2^c \\ 19.0 \pm 4.2^c \\ 11.7 \pm 0.3^b \\ 22.2 \pm 1.8^c \\ 6.45 \pm 2.44^a \end{array}$	

a-d) as in Table 2.

Table 4. Element Portions Extractable Using SM&T Sequential Extraction Procedure. Fraction 2 – Bound to Fe—Mn Oxides
(Extractable with 0.1 mol dm $^{-3}$ NH₂OH·HCl)

G - 11	Treatment	Mass fraction/(mg kg^{-1})			
5011		As	Cd	Pb	Zn
А	Control CaO CaCO $_3$ Zeolite natural Zeolite synthetic	$\begin{array}{l} 12.7\pm 0.6^{d}\\ 8.55\pm 0.67^{b}\\ 8.19\pm 0.11^{b}\\ 10.4\pm 0.6^{c}\\ 4.20\pm 0.13^{a} \end{array}$	$\begin{array}{c} 16.3 \pm 1.1^{a} \\ 16.1 \pm 0.5^{a} \\ 16.6 \pm 1.8^{a} \\ 15.5 \pm 0.9^{a} \\ 15.0 \pm 1.3^{a} \end{array}$	$\begin{array}{c} 1123 \pm 41^c \\ 920 \pm 14^b \\ 866 \pm 69^{ab} \\ 817 \pm 27^a \\ 815 \pm 19^a \end{array}$	$\begin{array}{r} 1438 \pm 74^b \\ 1352 \pm 29^b \\ 1350 \pm 75^b \\ 1169 \pm 198^a \\ 1271 \pm 49^{ab} \end{array}$
В	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 9.14 \pm 0.30^c \\ 7.21 \pm 0.50^b \\ 13.6 \pm 1.01^d \\ 7.67 \pm 0.20^b \\ 2.40 \pm 0.35^a \end{array}$	$\begin{array}{c} 3.32 \pm 0.19^c \\ 2.71 \pm 0.51^b \\ 3.62 \pm 0.22^c \\ 1.95 \pm 0.07^a \\ 1.57 \pm 0.04^a \end{array}$	$586 \pm 40^{d} \\ 506 \pm 33^{c} \\ 569 \pm 14^{d} \\ 425 \pm 43^{b} \\ 354 \pm 22^{a}$	$\begin{array}{l} 74.9 \pm 4.5^c \\ 60.7 \pm 5.6^{bc} \\ 77.0 \pm 17^d \\ 47.2 \pm 0.9^b \\ 30.7 \pm 1.5^a \end{array}$
С	Control CaO CaCO $_3$ Zeolite natural Zeolite synthetic	$\begin{array}{l} 9.35 \pm 0.84^c \\ 7.00 \pm 0.39^b \\ 7.42 \pm 0.60^b \\ 9.16 \pm 0.41^c \\ 2.12 \pm 0.32^a \end{array}$	$\begin{array}{c} 2.21 \pm 0.24^a \\ 2.63 \pm 0.26^b \\ 2.41 \pm 0.07^{ab} \\ 2.36 \pm 0.11^{ab} \\ 2.70 \pm 0.33^b \end{array}$	$523 \pm 19^{b} \\ 462 \pm 33^{a} \\ 460 \pm 33^{a} \\ 446 \pm 52^{a} \\ 421 \pm 17^{a} \end{cases}$	$\begin{array}{c} 17.9 \pm 1.3^{a} \\ 22.3 \pm 3.2^{b} \\ 17.1 \pm 0.4^{a} \\ 24.4 \pm 1.9^{b} \\ 17.8 \pm 2.2^{a} \end{array}$

a-d) As in Table 2.

extractable zinc (for control variants 9.3 % at soil A, 5.9 % at soil B, and 1.8 % at soil C). The extractability of both elements decreased by one order of magnitude at both limed and the synthetic zeolite treatments. These results correspond well with the results of Cd and Zn uptake obtained for different soils and plants [23—26]. The lowest effect on the extractability was reported for the application of the natural zeolite where the decrease did not exceed 30 % of the extractability in the control experiment. The effect of increased pH in the soil treated with the synthetic zeolite compared to the natural one was the important parameter in this case and possible differences in metal adsorption on zeolite surface must be taken into account. The better efficiency of synthetic zeolites compared to natural ones was explained by their higher purity [23].

Tables 3—5 present extractable with the extractable portions of elements in individual fractions determined by sequential extraction procedure. The composition of fraction 1, extractable with 0.11 mol dm^{-3} acetic acid, confirmed a higher extractability

g . 1	Treatment	Mass fraction/(mg kg^{-1})				
5011		As	Cd	Pb	Zn	
А	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 41.2 \pm 2.2^{b} \\ 39.8 \pm 3.2^{a} \\ 41.5 \pm 2.8^{b} \\ 42.6 \pm 3.1^{b} \\ 46.2 \pm 2.6^{c} \end{array}$	$\begin{array}{c} 2.31 \pm 0.05^a \\ 2.50 \pm 0.18^b \\ 2.52 \pm 0.27^{ab} \\ 2.40 \pm 0.16^{ab} \\ 3.21 \pm 0.46^b \end{array}$	$\begin{array}{l} 1193 \pm 22^{b} \\ 1157 \pm 49^{a} \\ 1206 \pm 77^{a} \\ 1267 \pm 56^{a} \\ 1211 \pm 85^{a} \end{array}$	$\begin{array}{r} 333 \pm 18^{a} \\ 356 \pm 28^{b} \\ 366 \pm 35^{a} \\ 352 \pm 1^{b} \\ 669 \pm 75^{a} \end{array}$	
В	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 7.24 \pm 0.36^{bc} \\ 6.19 \pm 0.58^{b} \\ 9.13 \pm 3.49^{c} \\ 3.10 \pm 0.83^{a} \\ 4.99 \pm 0.35^{ab} \end{array}$	$\begin{array}{l} 0.404 \pm 0.043^c \\ 0.358 \pm 0.094^{bc} \\ 0.438 \pm 0.063^c \\ 0.193 \pm 0.020^a \\ 0.281 \pm 0.042^{ab} \end{array}$	$\begin{array}{r} 366 \pm 36^{a} \\ 396 \pm 20^{ab} \\ 510 \pm 21^{c} \\ 425 \pm 23^{b} \\ 360 \pm 30^{a} \end{array}$	$\begin{array}{c} 35.6 \pm 2.8^{b} \\ 35.7 \pm 2.8^{b} \\ 32.2 \pm 2.7^{c} \\ 26.3 \pm 1.1^{a} \\ 31.1 \pm 6.1^{ab} \end{array}$	
С	Control CaO CaCO ₃ Zeolite natural Zeolite synthetic	$\begin{array}{l} 5.22 \pm 0.99^{ab} \\ 4.31 \pm 0.67^a \\ 3.84 \pm 0.66^a \\ 4.41 \pm 0.90^{ab} \\ 5.96 \pm 1.26^b \end{array}$	$egin{array}{l} 0.162 \pm 0.024^a \ 0.254 \pm 0.027^b \ 0.225 \pm 0.017^b \ 0.135 \pm 0.011^a \ 0.245 \pm 0.022^b \end{array}$	$\begin{array}{c} 268 \pm 16^{a} \\ 274 \pm 24^{ab} \\ 261 \pm 23^{a} \\ 303 \pm 13^{b} \\ 272 \pm 9^{ab} \end{array}$	$\begin{array}{c} 15.6 \pm 1.9^{ab} \\ 16.0 \pm 1.4^{b} \\ 14.2 \pm 1.2^{ab} \\ 15.7 \pm 2.4^{b} \\ 12.6 \pm 1.7^{a} \end{array}$	

a-d) As in Table 2.

of zinc and especially cadmium compared to that of arsenic and lead. The extractability of arsenic varied between 1 % (soil A) and 11 % (soil B) and the extractability of lead was between 1.5–3 % regardless of the experimental soil. Expectably, the application of an extraction agent stronger than $0.01 \text{ mol } \text{dm}^{-3}$ $CaCl_2$ and able to release the element portions described as "extractable" and "bound to carbonates" resulted in lower differences among individual soil treatments, especially at more mobile elements such as cadmium and zinc. The low pH of the extractant plays a significant role in this case as well. For arsenic, where the effect of pH on its availability is less significant, the effect of both zeolites was apparent, especially in the case of the synthetic one. This suggests that zeolites are able to create stronger bonds to the elements compared to liming where the soil pH is the predominant agent of element immobilization.

A decreasing availability of arsenic in the soils treated by the synthetic zeolite was also demonstrated in fraction 2 (extractable by 0.1 mol dm⁻³ NH₂OH ·HCl) representing the element portions bound to Fe—Mn oxides. The element portions extracted to fractions 2 and 3 showed some significant differences among individual treatments. However, the results did not reflect the effects of the treatments so clearly as in the case of the above-mentioned milder extractants. The percentage of immobilized elements was evidently rather low compared to element portions extractable from the contaminated soils in fractions 2 and 3. The high element contents in these samples obscured changes caused by the individual treatments.

An effective immobilization of Cd, Zn, and to lesser extent of Pb by the increase soil pH (liming) and sorption capacity (application of synthetic zeolite) was obtained after four vegetation periods. This suggests that these soil treatments have a stable effect for more than one vegetation period. In the case of arsenic, however, the liming was ineffective and a significant drop of its extractability was observed for zeolite treatments. Also, the influence of individual treatments differed for individual soils when the extent of the change of soil pH seemed to be the dominant parameter affecting the availability of cadmium and zinc. Evidently, these treatments are not generally acceptable for multicontaminated soils because the responses of cadmium and zinc to the soil treatments differed significantly from the behavior of arsenic. In the case of arsenic, other treatments are suitable for immobilization of this element in soil, e.g. recently tested iron grit combined with beringite showing promising results. Therefore, particular soil contaminants require specific approach [27]. Problems with applicability of the results from pot experiments to field conditions as discussed by *Friesl et al.* [3] (differences in rooting depth and density, spatial variability, varying soil moisture content, etc.) will be very important objective of further investigations.

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